

FINAL REPORT

January 31, 2004

**MICROGRAVITY STUDIES OF LIQUID-LIQUID PHASE
TRANSITIONS IN ALUMINA-YTTRIA MELTS**

**Flight Definition, Materials Science
Subdiscipline: Ceramics and Glasses**

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Principal Investigator: Dr. Richard Weber
Co-Investigator: Dr. Paul Nordine

Containerless Research, Inc.
Evanston, IL 60201-3149
Phone: 847/467-2678, Fax 847/467-2679
email: weber@containerless.com

COTR: Buddy Guynes
George C. Marshall Space Flight Center
Marshall Space Flight Center, AL 35812

Project Summary:

The scientific objective of this research is to increase the fundamental knowledge base for liquid-phase processing of technologically important oxide materials. The experimental objective is to define conditions and hardware requirements for microgravity flight experiments to test and expand the experimental hypotheses that:

1. Liquid phase transitions can occur in undercooled melts by a diffusionless process.
2. Onset of the liquid phase transition is accompanied by a large change in the temperature dependence of melt viscosity.

Experiments on undercooled YAG ($Y_3Al_5O_{12}$)- and rare earth oxide aluminate composition liquids demonstrated a large departure from an Arrhenian temperature dependence of viscosity. Liquid YAG is nearly inviscid at its 2240 K melting point. Glass fibers were pulled from melts undercooled by *ca.* 600 K indicating that the viscosity is on the order of 100 Pa·s (1000 Poise) at 1600 K. This value of viscosity is 500 times greater than that obtained by extrapolation of data for temperatures above the melting point of YAG. These results show that the liquids are extremely fragile and that the onset of the highly non-Arrhenian viscosity-temperature relationship occurs at a temperature considerably below the equilibrium melting point of the solid phases.

Further results on undercooled alumina-yttria melts containing 23-42 mole % yttrium oxide indicate that a congruent liquid-liquid phase transition occurs in the undercooled liquids. The rates of transition are inconsistent with a diffusion-limited process.

This research is directed to investigation of the scientifically interesting phenomena of polyamorphism and fragility in undercooled rare earth oxide aluminum oxide liquids. The results bear on the technologically important problem of producing high value rare earth-based optical materials.

Approach:

The research is focused on the study of undercooled pseudo-binary alumina-yttria melts. Containerless techniques are being used to access non-equilibrium liquids and allow precise control of melt chemistry at high temperatures. Although the oxides of interest are extremely stable and exhibit only small oxygen composition changes, some properties of melts are very sensitive to the ambient oxygen pressure which must be controlled in order to investigate subtle effects in liquid oxides.

Properties under investigation are the onset and kinetics of phase transitions in the liquid and the viscosity of the undercooled liquid as a function of the temperature. Earth-based research is being performed under conditions that meet some of the experimental constraints to provide the

design basis for microgravity experiments. Containerless experiments using aero-acoustic (AAL), aerodynamic (CNL) and electrostatic (ESL) levitation techniques achieve precise control of melt chemistry, access highly undercooled melts and glassy states, and control the effects of interaction with container walls on the evolution of morphology. Microgravity experiments will obtain the control of density-driven segregation, and especially of fluid flow required to test the experimental hypotheses and enable measurements of melt viscosity over the range of experimental conditions of interest.

Ground-based containerless experiments employ CRI's aero-acoustic and aerodynamic levitation facilities with CO₂ laser beam heating to investigate the effects of processing conditions on the compositions of interest. In these experiments, the melts are highly stirred by the aerodynamic and acoustic levitation forces and equilibrate rapidly with the process atmosphere. The experiments are performed in atmospheres with a controlled p(O₂), which (i) preserves the melt stoichiometry and avoids partial reduction of the oxides, and (ii) achieves conditions under which the liquid phase separation and glass formation occur in the YAG-composition liquid. Ground-based research using the ESL facility at NASA Marshall Space Flight Center (MSFC) is investigating the requirements for ESL experiments on oxides and defining boundary conditions for the flight experiments.

The requirements for flight experiments are described in the Draft Science Requirements Document. Detailed designs for the space-based microgravity experiments will be developed in collaboration with NASA scientists and engineers. This work may include low gravity experiments aboard parabolic aircraft flights if the ESL becomes available for this purpose.

Activities and Results:

The major activities during this project were to:

1. Investigation of phase transitions in selected YA-composition materials.
2. Sample preparation and planning for ESL experiments at MSFC.
3. Publication of results.
4. Complete an SCR.
5. Issue press release.

Analysis of Single and Two-phase Glasses:

Here we briefly present and discuss investigation of single- and two-phase glass materials formed from alumina-yttria compositions. More detailed reports are provided in previous NASA reports, the NASA Taskbook and our published and in-preparation papers.

SEM images of sectioned samples of YAG- and Y₂O₃ + 76 mole % Al₂O₃ (Y76A)-composition glasses are presented in Fig. 1. The YAG-composition glass is clearly 2-phase containing spheroidal precipitates that have the same chemical composition as the matrix. This result is consistent with the interpretation that the liquid undergoes a partial phase transformation prior to

vitrification. In more recent work we have concentrated on investigation of the Y76A materials that are at the limit of the glass forming range in the alumina-yttria system. As shown in Fig. 1, the Y76A-composition materials form a single phase glass core surrounded by a thin dendritic crust. SEM analyses performed by Dr. Greg Jerman at NASA MSFC indicate that the core has the same chemical composition as the batch of material used to make the samples. The crust consists of alumina dendrites and a Y-rich phase. Differential Scanning Calorimetry (DSC), see Fig. 2, shows that the Y76A glass exhibits a glass transition at approximately 1150 K followed by two exothermic events. The first exotherm releases about 40 % and the second about 50 % of the total heat released. Some additional heat is released during high temperature thermal events associated with densification of the crystalline phases.

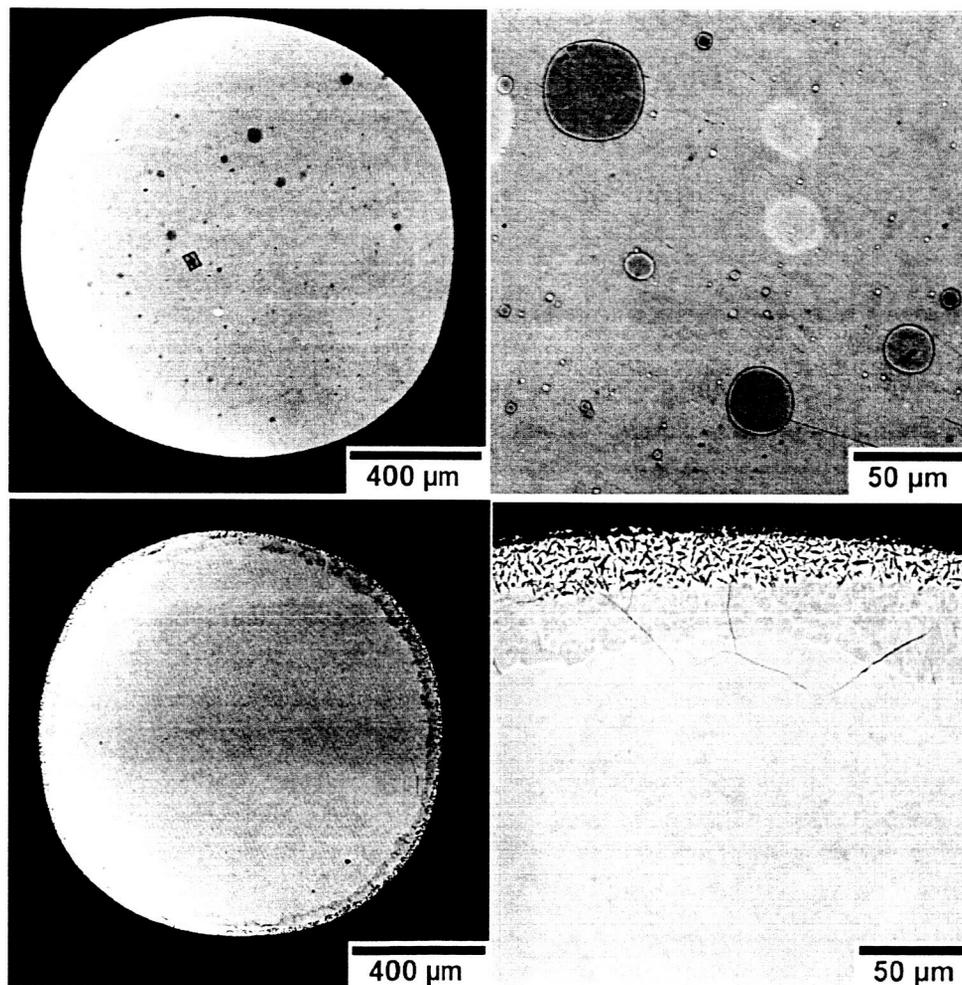


Fig. 1: Top left, SEM image of Y62.5A (YAG-composition) glass spheroid showing ‘droplet’ phase in amorphous matrix, top right, close-up image of the droplets in the glass matrix. Bottom left, SEM image of Y76A glass spheroid, showing crystalline surface layer and amorphous core, and bottom right, close-up image of the crystalline surface layer.

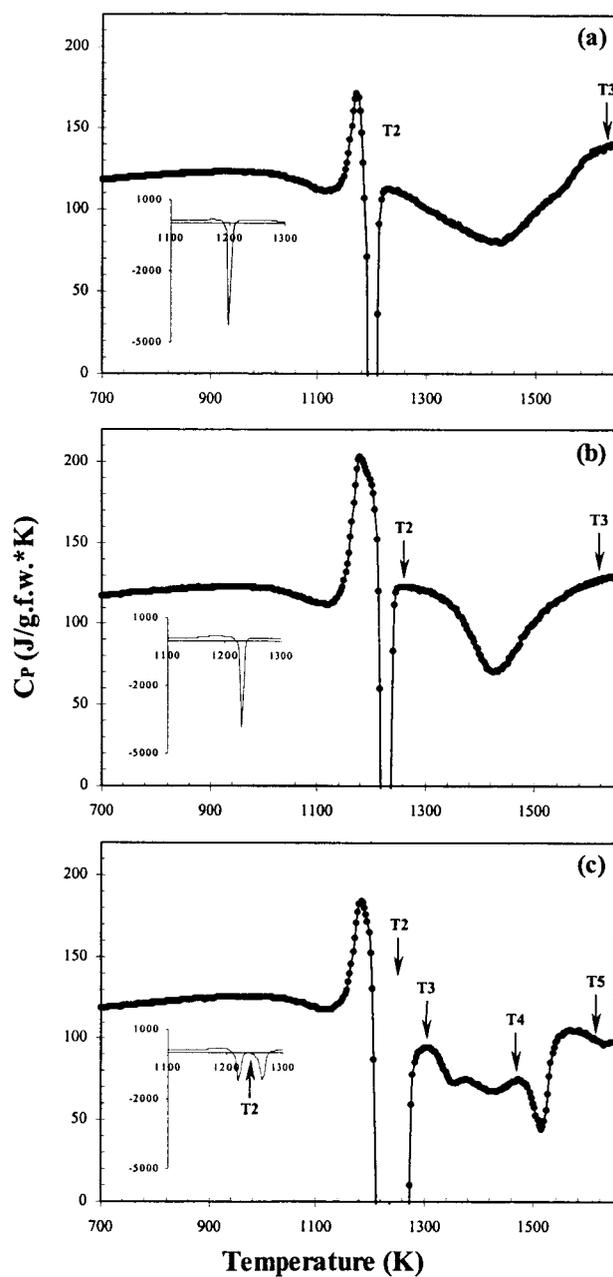


Fig. 2a-c: Differential scanning calorimetry (DSC) traces for (a) Y62.5A, (b) Y71.5A, and (c) Y76A, showing glass transition and exotherms. Insets show exotherms in their entirety; note the double exotherm for Y76A. Temperatures marked T2-T5 correspond to the temperatures at which samples were recovered for further analysis. (T1, not marked, corresponds to the as-made glass.)

X-ray diffraction analysis indicated that the materials are amorphous before and after the first exothermic event. The X-ray diffraction spectra show a few small peaks that could not be indexed, and were attributed to traces of crystals present in the as-made glasses. Nanocrystals of YAG (size ~ 18 nm) are formed in the second exothermic event, and grow to ~ 48 nm after heating to T5 ~ 1600K.

Density measurements showed a 10% increase in density, from 3.8 to 4.2 g/cm³, after heating the as-synthesized material to T2.

To further understand the nature of the effect that produces such a large evolution of heat during the first exotherm, heat treated samples were studied by high-field ²⁷Al NMR, neutron diffraction and transmission electron microscopy, results are shown in Figs. 3,4 and 5 respectively.

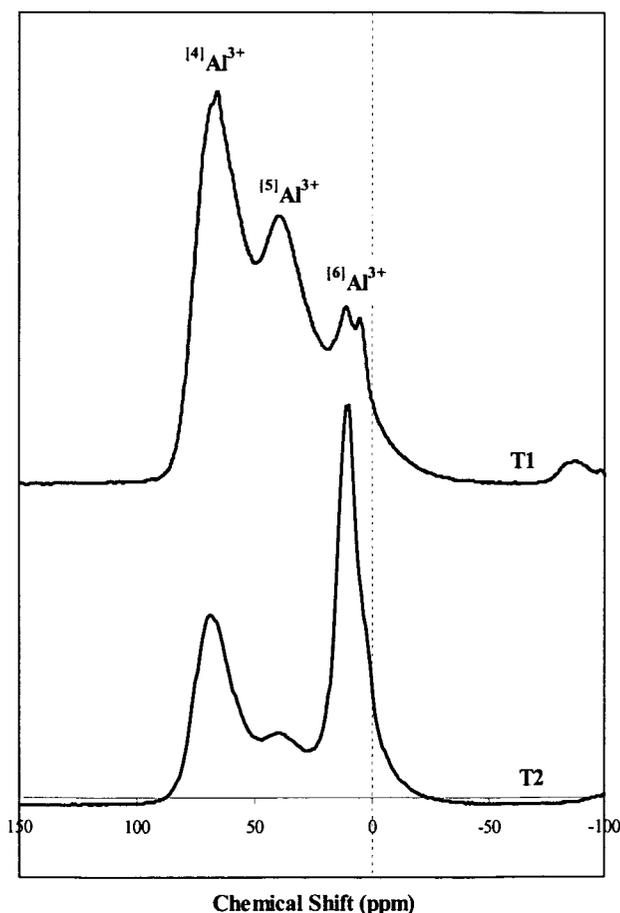


Fig. 3: High field ²⁷Al MAS NMR spectra for as-made (T1) and 'transformed' (T2) Y76A glass. T1 and T2 correspond to Y76A samples as illustrated in Figure 2c. Note the decrease in 4-coordinate and increase in 6-coordinate Al ions as a result of the structural rearrangements associated with the first exothermic event (T2) in Figure 2c.

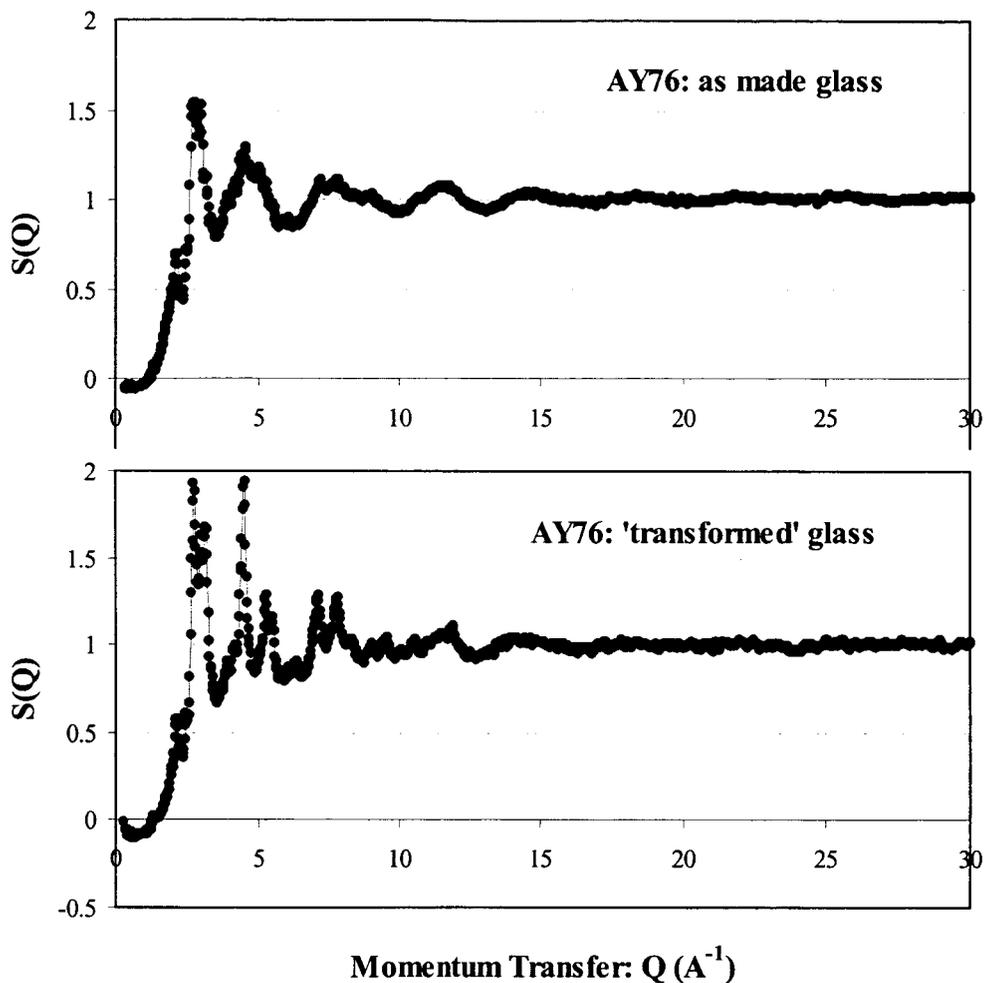


Fig. 4. Neutron diffraction spectra for the as-made and 'transformed' Y76A glasses. The peaks for the 'transformed' Y76A glass were indexed to cubic $\gamma\text{-Al}_2\text{O}_3$.

^{27}Al NMR reveals that heat treated glasses contains a much increased population of 6 coordinate aluminum ions compared to the as-made material. Neutron diffraction shows weak, broad Bragg peaks consistent with a nanophase component, indexing of the pattern indicates that the crystalline phases is metastable gamma-aluminum oxide. High resolution TEM imaging shows no evidence of crystals in the as-made glass core. After heating to T2, TEM shows a uniform distribution of nanoclusters of gamma-aluminum oxide in an amorphous matrix. If one assumes that the quantity of gamma alumina does not exceed that required to convert the matrix phase to the YAG composition, then the nanocrystalline gamma alumina would comprise up to 36 mol% of the sample on an M_2O_3 basis. Since (i) the transformed material density is $\sim 4.2 \text{ g/cm}^3$ and (ii) the density of gamma alumina and as-synthesized YAG-composition glass are both $\sim 4 \text{ g/cm}^3$, it appears that a polymorphic transformation of the matrix glass phase occurs together with the precipitation of gamma-alumina during the first exotherm.

The detailed analyses of the metastable materials made under well controlled conditions by containerless processing has led to a new understanding of the liquid state. We are proposing an interpretation of the results that links the phenomena of polyamorphism, formation of glacial phases similar to those reported in organic systems, and quasicrystallization that is seen in metallic alloys. These phenomena are related effects that occur when highly metastable systems move towards equilibrium. The structural rearrangements that occur do not lead to formation of bulk crystalline materials, as the liquid structure relaxes, crystal-like phases occur along with restructuring of amorphous phases. These new ideas are being written up for submission to the journal Nature.

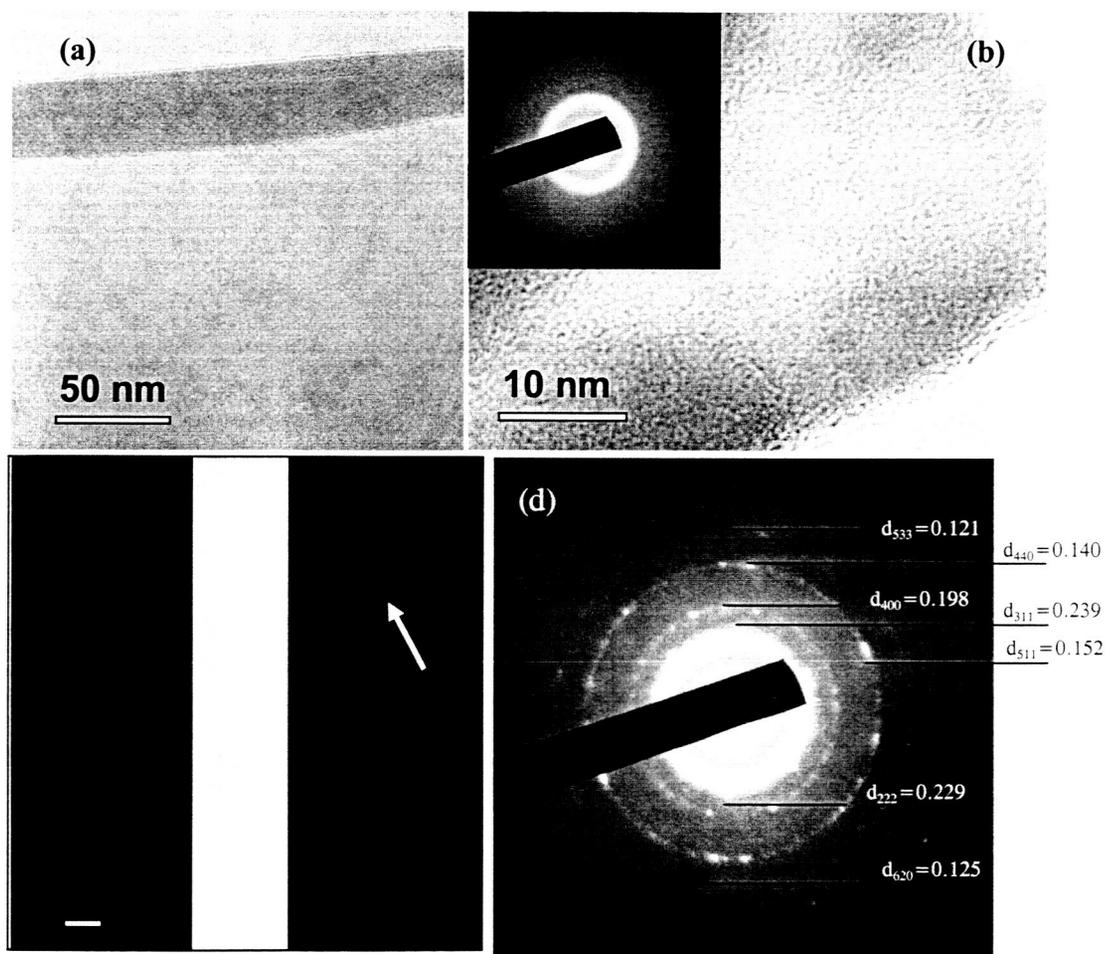


Figure 5a-d: High resolution TEM images of as-made (a, b) and transformed (c, d) glasses. The diffraction rings for the as-made glass (b) are characteristic of amorphous material. The diffraction rings (d) for the ‘transformed’ Y76A (c) were indexed to cubic gamma-Al₂O₃ and are characteristic of a nanophase material. The gamma-Al₂O₃ nanoclusters are seen as areas of dark contrast uniformly dispersed in the glass matrix, as shown in (c) the high-annual dark-field (HAADF)-STEM image.

Planned ESL Experiments at MSFC:

Dr. Richard Weber visited NASA Marshall Space Flight Center during a recent trip to Huntsville. Dr. Tom Rathz hosted a tour of the new high pressure ESL facility which is being commissioned at MSFC. Discussions about viscosity measurements were held with Dr. Jan Rogers who is in charge of the ESL and Dr. Robert Hyers from the University of Massachusetts Amherst. Dr. Jan Rogers and Robert Hyers will be in the Chicago area during a visit to Argonne National Laboratory in mid-August. A meeting to discuss ESL experiments was held.

CRI was selected for an NRA award to continue research on the oxide liquids. The new award NASA-NMM04AA23G is now in place. During this reporting period submission of several manuscripts was completed, a contract was made to engage Professor Robert Hyers at the University of Massachusetts Amherst to assist in measurements of melt density and viscosity that will be performed in the electrostatic levitator at Marshall Space Flight Center. Research towards the flight experiment is being continued under the new award.

Publication:

A total of 12 papers were published or are in process and approximately 20 presentations were made in connection with this project.

Press Release:

NASA and National Science Foundation will issue a joint press release on CRI's patented REAI™ Glass technology that was pioneered in this NRA projects. The press release has been written and is being processed, the NASA contact is Tracy McMahan (Media Writer (ASRI Inc.) NASA Marshall Space Flight Center, (256) 544-1634. tracy.mcmahan@msfc.nasa.gov). The release will be issued in mid-September with an associated press briefing at NASA Headquarters in Washington, DC.

Current problems

None

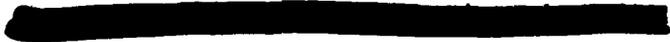
Work to be performed during next reporting period

The project is completed.

[REDACTED]

[REDACTED]

[REDACTED]


Estimated percentage of physical completion of project

The project is estimated to be 100% complete through the current reporting period.

Statement on cumulative costs and physical completion

The cumulative costs and physical completion of the project are approximately equal percentages of the total project cost and effort, respectively.

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